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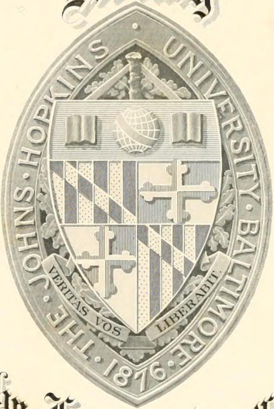

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William Jay
1895
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I. ORTHOCYANBENZENESULPHONIC ACID.

II. THE ACTION OF ALCOHOLS UPON THE HIGH-MELTING CHLORIDE OF ORTHOSULPHOBENZOIC ACID.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
BY
WILLIAM JAY KARSLAKE.

1895

71.261

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Part I: Orthocyanbenzenesulphonic Acid.

Introduction.

Ever since the preparation of the chloride of ortho-sulphobenzoic acid by Remsen and Dohme[1] in [illegible], there has been some doubt as to whether it was an individual substance to be expressed by one of the following formulas

$$C_6H_4 \left\langle {COCl \atop SO_2Cl} \right. \qquad C_6H_4 \left\langle {CCl_2 \atop SO_2} \right\rangle O$$

I II

or a mixture of both, as is now generally believed to be the case with phthalyl chloride. They, however, obtained no evidence of [illegible] and ascribed to it the symmetrical formula upon the ground that [illegible] the acid

---

[1] Am. Chem. Jour. XI-332;
[illegible];

obtained by treating it with alcohols under certain conditions. Two years later [illegible][1] in studying the action of aniline upon the chloride, obtained two isomeric and well characterized anilides the formation of which could not be very easily explained unless the chloride was regarded as a mixture made up of the two isomeric chlorides mentioned. In the following year [illegible] the behavior of the chloride towards various solvents [illegible] not a single individual. They succeeded in obtaining a partial separation into crystals which melted at 76° and [illegible] oil. They also found that of the two anilides, described by Remsen and [illegible]

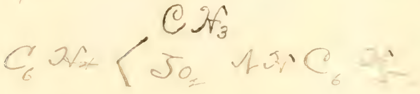
---

[1] [illegible] XIII
[illegible] 91;
[2] [illegible]

melting at 191° was formed [illegible] by [illegible] reaction, whereas the liquid chloride [illegible] d [illegible] melting [illegible] at 265°-270° [illegible] properties.

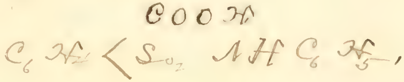
Moreover they showed it to be extremely probable that the solid chloride possesses the symmetrical formula. This they did as follows:-

Ort[illegible] [illegible] undoubtedly has the structure



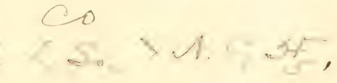
$$C_6H_4\left\langle\begin{matrix}CH_3\\SO_2NHC_6H_5\end{matrix}\right.$$

Upon oxidation this forms orthosul-phanilidobenzoic acid



$$C_6H_4<\begin{matrix}COOH\\SO_2NHC_6H_5\end{matrix},$$

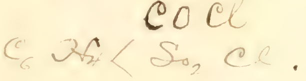
and this when heated, or when treated with phosphorus pentachloride, gives



$$C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>NC_6H_5,$$

which is identical with the one obtained by the action of aniline upon the solid chloride.

These reactions leave little doubt that the solid chloride is to be represented by the formula



$$C_6H_4<\begin{matrix}COCl\\SO_2Cl\end{matrix}.$$

Still later Remsen and Saunders[1] in a further study of the [illegible]

---

[1] Am. Chem. Journ. 17 347

of the chloride towards solvents succeeded in obtaining both chlorides, [illegible] the [illegible], [illegible] melting at 76°-77°, the other at [illegible]°

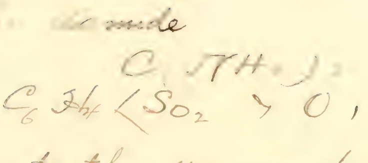
Both chlorides [illegible] acid when acted upon by water, but when heated with ammonia the products are different. It was found that the high melting chloride, which undoubtedly possesses the symmetrical formula [illegible] in [illegible] chloride thus,

$$C_6H_4\left\{\begin{matrix}CO\,Cl\\SO_2\,Cl\end{matrix}\right. + 4NH_3 = C_6H_4\left\{\begin{matrix}CO\\SO_2\end{matrix}\right\}NNH_4 + 2NH_4Cl$$

Unlike the low-melting chloride on the other hand, gave as the principal product a [illegible]

probability, as Mr. Chambers[I] of this laboratory has shown, is the ammonium salt of orthocyanbenzenesulphonic acid.

Remsen[II] had previously found that if the mixed chlorides were shaken for a few minutes in chloroform solution with [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] soluble in [illegible]. It [illegible] studying this reaction that [illegible] [illegible] the [illegible] - solution [illegible] [illegible] [illegible] [illegible] [illegible] to be the diamide

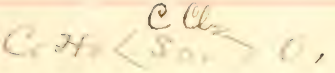


$$C_6H_4\left\langle\begin{matrix}C(NH_2)_2\\SO_2\end{matrix}\right\rangle O,$$

corresponding to the unsymmetrical chlorid

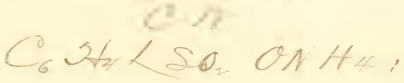
[I] Am. Chem. Jour. XVII – 251.

[II] Am. Chem. Jour. XVII – [illegible]



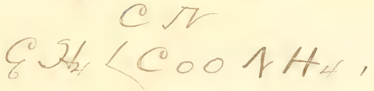
$$C_6H_4\begin{matrix}CCl_2\\SO_2\end{matrix}>O,$$

from which they were supposed to be obtained. Further study, however, showed that in all probability it was the ammonium salt of [illegible] of orthocyanbenzenesulphonic acid



$$C_6H_4\begin{matrix}CN\\SO_2ONH_4\end{matrix};$$

analagous to the ammonium salt of orthocyanbenzoic acid



$$C_6H_4\begin{matrix}CN\\COONH_4\end{matrix},$$

which Hoogewerff and Van Dorp[1] had obtained by heating phthalyl chloride in a [illegible] with aqueous ammonia. Presuming that the low-melting chloride has the unsymmetrical formula, its formation may be represented by the following

---

[1] Rec. Trav. Chim. [illegible]

equation.

$C_6H_4\left\langle\begin{matrix}CCl_2\\SO_2\end{matrix}\right\rangle O + 4NH_3 = C_6H_4\left\langle\begin{matrix}C\\SO_2\end{matrix}\right\rangle NH$
$+ 2NH_4Cl.$

No further studies, however, seemed desirable in order to prove the formation of the acid amid in ammonia beyond doubt, the work described in the following pages was taken up.

Preparation of Mixed Chlorides.

The method used at first for the preparation of mixed chlorides was essentially that given by Sanders¹. The acid potassium salt of ortho-sulphobenzoic acid, which in turn had been made from ammonium saccharin by the usual method²,

---

1) [illegible] 2) [illegible]

was treated with two molecules of phosphorus pentachloride and the resulting oily mass washed as well as possible with cold water. It was then solidified by surrounding it with a freezing mixture and further washed by repeated triturating with ice cold water in a mortar[1]. The chloride so obtained was then carefully dried on a porous plate and kept in a desiccator over calcium chloride. In spite of the great care taken in preparing the acid chloride by this method, a yield of only 40 to 50 per cent could be obtained, the remainder being recovered from the mother liquor in form of acid potassium salt upon evaporating to completely dryness

---

[1] The method of freezing washing was suggested by [illegible] of this Laboratory.

This suggested that either the water used in washing decomposed the chlorides to some extent or that some a disulphonic anhydride was formed in the action of the phosphorus pentachloride upon the acid potassium salt.

After several experiments the latter were found to be the [illegible] and by the following method almost theoretical yields are obtained.

The dry acid potassium salt was thoroughly mixed in a porcelain mortar with two and one-half molecules of phosphorus pentachloride. After the reaction had ceased the oily mass was poured into a flask and the phosphorus oxychloride distilled off under reduced pressure.

---

[1] [illegible]

The residual o-toluidine were then washed and dried as above mentioned. [illegible] [illegible] [illegible] [illegible] [illegible] used for the preparation of the ammonium salt of orthotoluidine- [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] mixed.

Preparation of [illegible] Orthotoluidine sulphonate.

A large number of [illegible] [illegible] [illegible] [illegible] the preparation of this salt [illegible] order to find those conditions which [illegible] give any thing like a satisfactory yield.

At first [illegible] [illegible]

[illegible] and washing them with dilute ammonia until a slight ammoniacal odor remained at the end of two or three [illegible]

The [illegible] [illegible] [illegible] small botryoidal masses composed of minute needles separated, together with some ammonium chloride and [illegible].

[illegible] aid of a suction-pump and carefully recrystallized from water. As thus obtained they are still never free from contamination with ammonium chloride?.

The yield is from five to ten per cent

The next method used was similar to [illegible] [illegible] [illegible] [illegible] [illegible] of [illegible] [illegible] except that dilute, instead of concentrated, ammonia was taken.

The [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible]. The [illegible] [illegible] of the solution [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] in the [illegible] 15 [illegible] of [illegible] [illegible] of [illegible] [illegible] was obtained.

The [illegible]

[illegible]

ether as the solvent and from 10 grams of mixed chlorides 1.6 grams of salt was obtained. The next method tried was one suggested by the same work, which Mr. Gray of this laboratory had done on the mixed chlorides of paranitroorthosulphobenzoic acid. By precipitating excess of silver nitrate to the dilute water solution obtained by extracting the chlorides with ether, filtering from the precipitate and evaporating to crystallization, a difficulty soluble silver salt of paranitroorthosulphobenzonitrile was obtained. This method, however, did not give satisfactory results when applied to this mixture of chlorides in [illegible]

is obtained which does not crystallize well. It had been noted in the above experiments that a considerable rise in temperature took place during the action of the ammonia upon the [illegible]. It was thought that this might [illegible] the yield of [illegible] [illegible] and the following [illegible] [illegible] [illegible] [illegible] [illegible] the method adopted in all later preparations of ammonia [illegible] [illegible] given in detail. 30 grams of mixed chloro[illegible] [illegible] dissolved in 125cc of ether and placed in a 500cc separating funnel. Finely Crushed ice was added and the [illegible] [illegible]

[illegible] the ether. About 1000 cc of ice-cold water was now added [illegible] [illegible] until a slight excess [illegible] of about two [illegible]. [illegible] added so that there was always some present. The water solution was now drawn off, washed once or twice with ether, filtered, and [illegible] the water bath, [illegible] was obtained which is a yield of 30 per cent. Generally, however, the yield obtained by this same method in later experiments was

from 20 to 25 per cent. A word must also be said in regard to the crystallization of solutions from which the ammonium orthocyanbenzenesulphonate is to be obtained. At first the ammoniacal water solution was [illegible] salt of saccharin [illegible] with the ammonium orthocyanbenzenesulphonate. The mass thus obtained, after being drained by the aid of the suction pump, was placed in a beaker and treated with small quantities of cold water [illegible] and the ammonium salt of saccharin much more rapidly [illegible]

the compact nodules of the ammonium orthocyanbenzenesulphonate. At the best, however, this is a poor method of separation, although at times, as later, it was found advantageous to resort to it. The method of heating the acid-mixture until perfectly dry, moistening with absolute alcohol, filtering from the ammonium [illegible] and evaporating to crystallization was also tried but did not give satisfactory results. It was found that the best and most satisfactory method consisted in evaporating the solution to such a concentration that [illegible] perfectly cold solution and stood

[illegible]

It seems that considerable time is required for the ammonium orthocyanbenzenesulphonate to arrange itself in crystalline form; that it has a tendency to form a supersaturated solution. It was frequently noticed that if the solution was too concentrated the ammonium chloride and the ammonium salt of saccharin would separate first, while, if the same solution was not so concentrated the ammonium orthocyanbenzenesulphonate separated first. As thus obtained, however, by the above described method, the salt is still very far from pure, being contaminated with a large quantity of some chlorine compound from which it is extremely difficult to [illegible].

[illegible]
[illegible] that it was ammonium
[illegible]
[illegible]
ammonium chloride was present
still a further study in regard
to this point seems desirable
in order to find out if only
[illegible] chloride [illegible] present.
After a large number of
experiments it was found that
[illegible]
absolute alcohol [illegible]
[illegible]
even by this method, at least
[illegible] 6 crystallizations [illegible].
Repeated recrystallizations from
absolute alcohol [illegible]
[illegible]

The chloride obtained and crystallized was from alcohol in beautiful transparent needles arranged in rosettes, while from water it separated in rectangular [illegible] plates. [illegible] It is [illegible] soluble in [illegible] [illegible] [illegible] and hot alcohol, but much less so in cold alcohol, from which it crystallizes best. It melts at [illegible] °C uncorrected. Upon comparing some of this [illegible] with [illegible] Mr. Thomson [illegible] it was found identical in every respect. Of the preparation,

I 0.2014 gr. gave 0.2376 gr. $BaSO_4$ 16.11% S.

II 0.1988 gr. gave 25.80 C.C. nitrogen at 24°C. and [illegible] M.M. = 14.58%

III 0.2125 gr. gave 0.2490 gr. $BaSO_4$ 16.10% S.

Calculated for $C_6H_4<^{CH_3}_{SO_2ONH_4}$			Found I	II	III
$C_7H_8O_3$	140	70.00			
S	32	16.00	[illegible]		[illegible]
N	28	14.00	—	14.58	—
	200	100.00			

Analysis I and II are those of Mr. Chambers. The nitrogen was determined by the absolute method and the sulphur by the Carius method.

In several experiments [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] the [illegible] orthosulph[illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible]

They were first obtained from a solution of ammonium [illegible] which had been put in a desiccator [illegible] uric [illegible] [illegible] the cold. They were [illegible] obtained from a solution of 0.8 gram [illegible] which had been dissolved in 20 cc of water and boiled with a return condenser for 2½ hours.

Lastly, they were obtained, and then in large quantities, upon [illegible] the first [illegible] solution in order to obtain the first deposit of the ammonium orthocyanbenzenesulphonate.

The plates were mechanically separated and dissolved in water for recrystallization. These [illegible]

not the biuret, but ammonium orthocarbobenzenesulphonate in its well known form. Of the four plates which were obtained in the first observation,

I 0.4655 gr. gave 0.5600 gr. $BaSO_4$ = 16.52% S.
II 0.4060 gr. gave 0.4735 gr. $BaSO_4$ = 16.02% S.

They suffered no loss upon heating to 110°C. The sulphur determinations were made by the [illegible]

Repeated experiments under apparently the same and other conditions were made in order to obtain enough of the salt for a complete analysis, but they were not obtained again. From these four determinations and from the analyses, it would seem however that they were another crystal [illegible]

form of ammonium orthocyanbenzenesulphonate but further studies upon this point is required.

Sodium Salt, $C_6H_4<\begin{array}{l}CN\\SO_2ONa\end{array} + H_2O$.

This salt has already been described by Remsen[1] who made it by heating orthocyanbenzenesulphone chloride with sodium hydroxide. It is made by treating one molecule of the ammonium salt with one molecule of sodium hydroxide and evaporating to crystallization upon the water bath.

It crystallizes from [illegible] in large transparent prismatic plates containing one molecule of water of crystallization.

Of the [illegible],

I 0.2097 gr. gave 0.2227 gr. [illegible]

II 0.1134 gr. gave 0.1193 gr. [illegible]

---

[1] (Ber. XXVI - 3 [illegible])

III 0.2278 gr. gave 0.2372 gr. $BaSO_4$ = 14.62 % S

IV 0.1920 gr. lost 0.0158 gr. at 150° = 8.23 % H_2O, and gave 0.0613 gr. Na_2SO_4 = 10.34 % Na.

Calculated for $C_6H_4<^{CN}_{SO_2}ONa + H_2O$.			Found I	II	III	IV
$C_7H_4NO_3$	150	67.27				
S ~~Na~~	32 ~~23~~	14.35	14.57	14.55	14.62	
Na ~~S~~	23 ~~32~~	10.31				10.34
H_2O	18.	8.07	—	—	—	8.23
	223.	100.00				

There was no further loss in weight upon heating to 175°C. Analysis I is that of Mr. Chambers of the salt which he made.

Potassium Salt $C_6H_4<^{CN}_{SO_2}OK$.

This salt is made by treating the ammonium salt with [illegible]

concentrated solution of potassium cyanide. It is much more soluble than the corresponding ammonium salt separating from moderately dilute solutions in small transparent needles [illegible] from [illegible] [illegible] [illegible] the [illegible] salt. It is very easily prepared. Of these crystals

I 0.2128 gr. gave 0.0830 gr. K_2SO_4 = 17.61 % K.
II 0.2295 gr gave 0.0903 gr K_2SO_4 = 17.66 % K.
III 0.2550 gr gave 0.2824 gr $BaSO_4$ = 15.22 % S.

Calculated for			Found.		
$C_6H_4<^{CN}_{SO_2OK}$			I	II	III
$C_7H_4NO_3$	150				
S	32	15.16			15.22
K	39.1	17.67	17.61	17.66	
	221.1				

The salt lost nothing in weight upon heating to 190°C.

Barium Salt $(C_6H_4\langle^{CN}_{SO_3})_2Ba \cdot 2H_2O$.
Considerable difficulty was experienced in obtaining this salt pure, so that further study upon it is desirable. There seemed to be a strong tendency for the nitrile group to undergo saponification, thereby [illegible] rise to [illegible]. The analyses given below are of some crystals which were obtained in the attempt to prepare the free acid, and which were obtained by treating the ammonium salt with only three-quarters of the calculated quantity of barium hydroxide and [illegible] heating [illegible] the [illegible]

until no more ammonia was given off. It was then filtered, concentrated to small bulk and crystallized from dilute alcohol. It separated in little tufts composed of white silky needles. These were washed with alcohol to free them from any ammonium salt that might be present. Of the air dried crystals,

I 0.1065 gr. gave 0.0459 gr. $BaSO_4$ = 25.34 % Ba

II 0.1187 gr. gave 0.0512 gr. $BaSO_4$ = 25.36 % Ba

III 0.1006 gr. lost 0.0070 gr. at 105° = 6.96 % H_2O and gave 0.0438 gr. $BaSO_4$ = 25.59 % Ba

Calculated for $(C_6H_4\left(\begin{smallmatrix}CN\\SO_3\end{smallmatrix}\right)_2Ba+2H_2O$			Found I	II	III
$C_{14}H_8N_2O_6$	300.				
Ba	137.	25.51	25.34	25.36	25.59
$2H_2O$	36.	6.71			6.96
	473				

As stated above this salt was used in the attempt to prepare free orthocyanbenzenesulphonic acid. It was dissolved in water and dilute sulphuric acid carefully added until no further precipitation of barium sulphate took place. It was then filtered, evaporated to small bulk upon the water-bath and placed in a desiccator over sulphuric acid. A syrupy transparent mass was obtained which slowly solidified into many fine needles arranged in rosettes. These were then washed with ether containing a little alcohol and finally with ether alone. They melted at 180°-183° uncorrected.

Of the crystals,

0.1880 gr. gave 0.2037 gr. BaSO4 = 14.91% S

The[1] formulas $C_6H_4<^{CN}_{SO_2\ OH} + 2H_2O$,

$C_6H_4<^{CONH_2}_{SO_2\ OH} + H_2O$, and

$C_6H_4<^{COONH_4}_{SO_2\ OH}$,

all agree for 14.62 % S. by theory. Upon comparison however of its melting point and method of crystallization with the ortho-carbaminsulphonic acid described by Fahlberg and Remsen and by Remsen[2] there can be little doubt of the identity of the two substances. Therefore its formula is

$$C_6H_4<^{CONH_2}_{SO_2\ OH} + H_2O.$$

Not enough of the salt was obtained for a water determination.

---

[1] Ber. XII - 750; [2] Loc. cit.

Other attempts were made to isolate the free acid by other methods [illegible] also failed to isolate it.

Transformation of Orthocyanbenzenesulphonic Acid into Orthobenzaminesulphonic Acid.

The transformation was [illegible] effected by boiling with excess of dilute [illegible]. [illegible] that in the preparation of the above described cyan-salts, great care is necessary in using no more than calculated quantity of base. In most cases the reaction [illegible] to the following [illegible]

$$C_6H_4 \left\langle \begin{matrix} CN \\ SO_2OH \end{matrix} \right. + H_2O = C_6H_4 \left\langle \begin{matrix} CONH_2 \\ SO_2OH \end{matrix} \right.$$

and there stops, no further hydrolysis taking place to produce the corresponding ammonium salt as here represented:

$$C_6H_4 \left\langle \begin{matrix} CONH_2 \\ SO_2OH \end{matrix} \right. + H_2O = C_6H_4 \left\langle \begin{matrix} COONH_4 \\ SO_2OH \end{matrix} \right.$$

There were a few salts obtained, however, to which no formulae could be assigned.

Ammonium Salt $C_6H_4 \left\langle \begin{matrix} CN \\ SO_2ONH_4 \end{matrix} \right.$. This salt has already been prepared by Fahlberg and Barge[1] and described as crystallizing from alcohol in [illegible] which melt at 255°–256°. Remsen[2] describes it later as crystallizing

form [illegible] [illegible] prismatic crystals containing one molecule of water of crystallization. These descriptions do not agree with the salt I obtained by boiling 3 grams of ammonium [illegible] with dilute hydrochloric acid and for 8 hours with a return condenser. Upon concentrating to dryness when the water had several times to drive off most of the hydrochloric acid. There was obtained by crystallization from a water solution clear transparent needles which contained no water of crystallization and which melted at 219°-220° uncorrected. A sulphur determination was made by the Liebig method.

Of the crystals

0.1913 gr gave 0.2058 gr. $BaSO_4$ = 14.74% S

The formula $C_6H_4\left<\begin{matrix}CONH_2\\SO_2ONH_4\end{matrix}\right.$ requires 14.65 %

This work requires further study.

Potassium Salt. $C_6H_4\left<\begin{matrix}CONH_2\\SO_2OK\end{matrix}\right.+H_2O$

This salt was made by boiling with a return condenser 3 grams [illegible] cyan salt [illegible] (5 grms) of dilute potassium hydroxide for 5 hrs. From a moderately concentrated solution there separated transparent [illegible] prisms which [illegible]

[illegible]

of these crystals,

I 0.2409 gr. lost 0.0169 gr. below 135° 7.01% H

II 0.1427 gr lost 0.0119 gr below 135° 6.88% H_2

and gave 0.0588 gr. K_2SO_4 = 15.38 % K.

III 0.1105 gr. gave 0.0376 gr. K_2SO_4 = 15.32 %

Calculated for $C_6H_4\left<{CO\,NH_2 \atop SO_2\,OK}\right. + H_2O$		Found I	II	III
K	15.29		15.38	15.32
H_2O	7.00	7.01	6.88	

There was no further loss in weight upon heating to 2[illegible]0 °C

Sodium Salt $C_6H_4\left<{CO\cdot NH_2 \atop SO_2\cdot ONa}\right. + 2H_2O$

This salt was made just as the corresponding potassium salt by using sodium hydroxide, and was found [illegible]

in transparent prismatic plates from moderately concentrated solutions of the crystals.

I 0.3653 gr. lost 0.0509 gr. below 150° = 13.95% H_2O,
and gave 0.1002 gr. Na_2SO_4 = 8.89% Na.
II 0.1894 gr. lost 0.0263 gr. below 150° = 13.88% H_2O,
and gave 0.0533 gr. Na_2SO_4 = 9.12 % Na.

Calculated for $C_6H_4<\begin{smallmatrix}CONH_2\\SO_2ONa\end{smallmatrix} + 2H_2O$		Found I	II
Na	8.88	8.89	9.12
$2H_2O$	13.85	13.95	13.88

No further loss in weight occurred upon heating to 185°.

Barium Salt ($C_6H_4\begin{pmatrix}CONH_2\\SO_3O\end{pmatrix}_2Ba\,5H_2O$)

This salt was made by boiling the ammonium ——— cyanic acid for 5 hours with a large excess of barium hydroxide. The excess of barium hydroxide was then precipitated with carbon dioxide and the filtered solution evaporated to small bulk. It was found that crystallization did not easily take place from syrupy solutions, while from dilute alcohol it separated in white transparent needles grouped in rosettes. Of these crystals

I 0.2490 gr gave 0.0928 gr. $BaSO_4$ = 21.90 % Ba

II 0.3375 gr lost 0.0477 gr. below 110° = 14.1 % H_2O

and gave 0.1262 gr. $BaSO_4$ = 21.98 % Ba

III 0.2169 gr gave 0.[illegible] gr. $BaSO_4$ = [illegible]

IV 0.2596 gr. lost 0.0386 gr. [illegible] [illegible] % H_2O

Calculated for $(C_6H_4<^{COO}_{SO_3}>H)_2Ba + 5H_2O$		Found I	II	III	IV
Ba	21.65	[illegible]	[illegible]	[illegible]	
$5H_2O$	14.35			[illegible]	[illegible]

No further loss in weight took place upon heating to 145°C.

A Calcium Salt was made in the same manner as the corresponding barium salt, and was found to crystallize in transparent needles. The analysis gave 10.34% Calcium and 19.58% water lost at 145°C. As no formula was found to agree with these results it will require further study.

A Basic Lead Salt was also made, for which no formula could be deduced. It was made by heating the [illegible] upon the water bath until large masses of finely precipitated lead hydroxide settled and the ammonia was given off and then filtered. Upon cooling there separated crystals composed of white needles arranged [illegible] in [illegible]. It was dried [illegible] and weighed after heating to 140° and gave the following results:

I 0.2349 gr gave 0.2068 gr $PbSO_4$ = 59.34% Pb

II 0.1658 gr gave 0.1440 gr $PbSO_4$ = 59.33 [illegible]

III 0.1860 gr gave 0.1614 gr $PbSO_4$ = [illegible]

IV 0.[illegible]35 gr gave 0.1634 gr $PbSO_4$ [illegible]

I 0.2772 gr. gave 0.1634 gr. $PbSO_4$ = 6.22% S.

Analysis III was of a second preparation of the salt. The lead was determined by ignition of the salt with addition of sulphuric acid and the sulphur by the Carius method.

Transformation of Orthocyanbenzenesulphonic Acid into Orthosulphobenzoic Acid.

This was accomplished by heating 2 grams of the potassium salt with 15cc of hydrochloric acid (2:1) in a sealed tube for 6 or 7 hours at 190°C. Upon evaporating to crystallization, the characteristic rhomboidal plates of the acid potassium salt of orthosulphobenzoic acid separated.

Of these crystals,

0.2529 gr. gave 0.2827 gr. $BaSO_4$ = 14.64% S

The formula $C_6H_4 < \overset{COOH}{SO_2OH}$ requires 14.61% Sulphur.

To further identify this salt the corresponding potassium salt was prepared by treating it with slight excess of potassium hydroxide then acidifying with hydrochloric acid and allowing to crystallize.
The well known orthorhombic plates of the acid potassium salt of orthosulphobenzoic acid were obtained, of which,
0.2839 gr. gave 0.1033 gr. K_2SO_4 = 16.33% K

The formula $C_6H_4 < \overset{COOH}{SO_2OK}$ requires [illegible] Potassium.

Conclusion

From this investigation it is clearly evident that there is little doubt that orthocyanbenzenesulphonic acid is formed as one of the products of the action of ammonia upon the mixed chlorides of orthosulphobenzoic acid. Moreover, its formation can hardly be explained upon any other hypothesis than that it is derived from a chloride possessing the unsymmetrical formula

$$C_6H_4 \left< \begin{matrix} CCl_2 \\ SO_2 \end{matrix} \right> O.$$

If this be so, it appears highly probable that by the action of ammonia on [illegible] would in part form [illegible] [illegible] [illegible]

under the existing conditions goes over by intramolecular change into orthosulphobenzoic acid, thus

$$C_6H_4{<}\begin{matrix}CCl_2\\SO_2\end{matrix}{>}O \rightarrow C_6H_4{<}\begin{matrix}C=NH\\SO_2\end{matrix}{>}O \rightarrow C_6H_4\begin{matrix}C:N\\SO_2OH\end{matrix}$$

Part II – The Action of Alcohols upon the High-melting Chloride of Orthosulphobenzoic Acid.

Introduction.

As already mentioned in the introduction of Part I Remsen and Dohme studied the action of alcohols upon the chloride of orthosulphobenzoic acid, which at that time was believed to

to a single substance. Subsequent investigation, however, having shown it to be a mixture, it seemed very desirable that these should be supplemented by a study of the action of alcohol upon the high-melting chloride and upon the low-melting chloride of which this mixture had been shown to be composed. Since large quantities of the high melting chloride were obtained as a by-product in the preparation of orthobenzoic-sulphinide, the study of the action of alcohol upon the chloride was taken up conjointly with the investigation described.

Preparation of High melting Chloride.

The ether or chloroform solution obtained in the preparation of ammonium orthocyanbenzensulphonate is dried with calcium chloride, filtered and evaporated to crystallization. Beautiful transparent prismatic needles or blades are obtained which, after recrystallization from ligroine (b.p. 105°-140°), melt at
°C. The yield — 25-30 per cent.

Acid Esters of Orthosulphobenzoic Acid and Some of Their Salts.

Practically the same results were obtained [illegible]

the chloride with boiling alcohols the more [illegible] by heating and alone. Acid esters are formed according to the following equation:

$$C_6H_4<^{COCl}_{SO_2Cl} + 3\,ROH = C_6H_4<^{COOR}_{SO_2OH} + 2\,HCl + R_2O$$

The best results were obtained as follows:- The chloride was boiled with excess of alcohol in a small flask connected with a return-condenser for several hours. The excess of alcohol was then distilled off, a new portion of alcohol added, and the whole boiled again for about the same length of time. This was repeated until a [illegible]

when permanganate [illegible] gave no [illegible] permanent [illegible], or until the solution in the flask was almost free from hydrochloric acid as shown by testing a little with silver nitrate.

The acid esters as then obtained are colorless oily liquids which are sparingly soluble in water. None of them at least by this method were obtained in the crystalline condition. All of them undergo partial saponification when treated with water. The presence of a little alcohol however hinders this very materially. These esters were [illegible] [illegible] by means of [illegible] [illegible] them.

Acid Methyl Ester $C_6H_4 < \begin{matrix} COOCH_3 \\ SO_3OH \end{matrix}$.

This was made according to the method mentioned. It does not apparently differ from that obtained by Remsen and Dohme. As will be seen later, it was probably obtained in a [illegible] condition in the solid condition by another method. The following salts were made.

Silver Salt $C_6H_4 < \begin{matrix} COOCH_3 \\ SO_3OAg \end{matrix}$.

This was made by treating the acid methyl ester with silver carbonate, adding a little methyl alcohol and evaporating to crystallization upon the water bath. It separates in large [illegible]

which was very soluble in water.
Although the solution showed some decomposition due to exposure to light, the salt was easily obtained. It agrees with the salt described by Remsen & [illegible].
Of the crystals,
0.[illegible] gr. gave 0.[illegible] gr. [illegible] Ag

Calculated for $C_6H_4<^{COOCH_3}_{SO_2OAg}$	Found
Ag 33.41	33.61

Calcium Salt, $(C_6H_4<^{COOCH_3}_{SO_2O})_2Ca$ [illegible]
This was made in the same manner as the corresponding silver salt. [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible]

needles arranged in rosettes.
Of the crystals,

I 0.[illegible] gr lost 0.00[illegible] gr below [illegible]°C 3.57% H_2O
and gave 0.0556 gr $CaSO_4$ = 8.20% Ca
II 0.[illegible] gr gave 0.06[illegible] gr $CaSO_4$ = 8.23% Ca.

Calculated for $(C_6H_4<^{COOCH_3}_{SO_2O})_2Ca+H_2O$		Found I	II
Ca	8.19	8.20	8.23
H_2O	3.69	3.57	

Copper Salt $(C_6H_4<^{COOCH_3}_{SO_2O})_2Cu+4H_2O$
It crystallizes from concentrated solutions in light blue prismatic needles arranged concentrically in groups. The copper was determined electrolytically.

Of the crystals

I 0.1898 gr. lost 0.0247 gr below 100° – 12.49 % H_2O

And gave 0.0218 gr. Copper 11.48 % Cu

II 0.1685 gr. lost [illegible] gr below 100° [illegible] % H_2O

And gave 0.0190 gr. Copper = 11.27 % Cu.

Calculated for $(C_6H_4<^{CO\cdot NH_2}_{SO_2\cdot O})_2Cu + ~~4H~~ 4H_2O$		Found I	Found II
Cu	11.26	11.48	11.27
$4H_2O$	12.73	13.39	13.[illegible]0

Strontium Salt $(C_6H_4<^{CO\cdot OCH_3}_{SO_2\cdot O})_2Sr + 8H_2O$. This crystallizes in beautiful transparent plates from concentrated solutions. Of the crystals

0.2810 gr. gave 0.0774 gr. $SrSO_4$ 13.13 % Sr

Calculated for $(C_6H_4<^{COOCH_3}_{SO_2O})_2Sr+5H_2O$	Found
Sr 13.14	13.13

Nickel Salt, $(C_6H_4<^{COOCH_3}_{SO_2O})_2Ni+6H_2O$. This crystallizes in transparent green plates from concentrated solutions. Of the crystals,

0.2282 gr. gave 0.0222 [illegible] 9.77 %

Calculated for $(C_6H_4<^{COOCH_3}_{SO_2O})_2Ni+6H_2O$	Found
Ni 9.67	9.77

The [illegible] [illegible] [illegible]

[illegible]

Manganese Salt. $(C_6H_4<^{CO \cdot OCH_3}_{SO_2 \cdot O})_2Mn + 4H_2O$

This crystallizes in very clear transparent plates from concentrated solutions. Of the crystals

0.1618 gr. gave 0.0214 gr. Mn_3O_4 = 9.78% Mn

Calculated for $(C_6H_4<^{COOCH_3}_{SO_2 \cdot O})_2Mn + 4H_2O$	Found
Mn 9.85	9.70

Magnesium Salt $(C_6H_4<^{COOCH_3}_{SO_2 \cdot O})_2Mg + 6H_2O$

This crystallizes in large transparent plates. Of the crystals

0.3161 gr. gave 0.0684 gr. $MgSO_4$ = 4.32% Mg

Calculated for $(C_6H_4<^{COOCH_3}_{SO_2 \cdot O})_2Mg + 6H_2O$	Found
Mg. 4.24	4.32

Barium Salt, which crystallizes in white needles [illegible]

The Zinc salt, which crystallizes in thin transparent plates; the ammonium salt, which crystallizes in thin broad needles; and the lead salt which crystallizes in thin plates were obtained but for lack of time were not analyzed.

Acid Ethyl Ester $C_6H_4 < \begin{matrix} CO_2C_2H_5 \\ SO_2OH \end{matrix}$

This was made in precisely the same way as the acid methyl ester. Although not obtained in crystalline condition by this method it was probably obtained then in another method. It does not differ apparently from that obtained by Fahlberg.

The following salts were made.

Barium Salt. $(C_6H_4<^{COOC_2H_5}_{SO_2O})_2Ba$.
This was made by treating the acid ethylate with barium carbonate, adding a little ethyl alcohol and evaporating to crystallization upon the water bath. It crystallizes in groups of small needles arranged in rosettes as described by Remsen & Dohme. Of the desiccator dried crystals, 0.1436 gr lost no weight upon heating to 200°C, and gave 0.0558 gr. $BaSO_4$ - 22.85% Ba.

Calculated for $(C_6H_4<^{COOC_2H_5}_{SO_2O})_2Ba$		Found
Ba	23.[illegible]	[illegible]

the formula [illegible] describes the salt as containing 4 molecules of water of crystallization, it evidently loses it when dried in a desiccator.

The Potassium salt which crystallizes in needles; the copper salt which crystallizes in fine silky light blue needles, and the magnesium salt, were made but were not analyzed for lack of time.

Acid Normal Propyl Ester $C_6H_3\left\langle\begin{matrix}COOC_3H_7\\SO_3H\end{matrix}\right.$

This was prepared in the same manner as the other acid esters and possesses the same general properties. The barium salt was made

Barium Salt $(C_6H_4{}^{COOC_3H_7}_{SO_3})_2Ba+2\frac{1}{2}H_2O$

The salt crystallyzes in needles arranged more or less in rosettes. The salt loses two molecules of water of crystallzation when dried in a desiccator. Of the air dried crystals.

0.1891 gr gave 0.0674 gr $BaSO_4$ = 20.45% Ba

of the desiccator dried salt,

0.1172 gr. lost 0.0051 gr. below 110°C = 4.36% H_2O

and gave 0.1452 gr. $BaSO_4$ = 21.46% Ba

Calculated for		Found
$(C_6H_4{}^{COOC_3H_7}_{SO_3})_2Ba+2\frac{1}{2}H_2O$		
Ba	20.51	20.45
$(C_6H_4{}^{COOC_3H_7}_{SO_3})_2Ba+\frac{1}{2}H_2O$		
Ba	21.67	21.46
H_2O	4.4[illegible]	4.36

Chlor-Esters of Orthosulphobenzoic Acid.
In preparing these it was found that by continued action of cold alcohol upon the chlorides the reaction went further than that expressed by the following equation.

$$C_6H_4<^{COCl}_{SO_2Cl} + ROH \quad C_6H_4<^{COOR}_{SO_2Cl} + HCl$$

Two portions of chloride were dissolved in cold absolute methyl alcohol and in cold absolute ethyl alcohol respectively. Upon allowing the solution to stand some time and the alcohols to evaporate spontaneously, oils were obtained, mixed with some crystals of chloride which had been unacted upon.

They were repeatedly redissolved in their respective alcohols and allowed to evaporate spontaneously until crystals of solid chloride ceased to appear. In this manner oils were obtained as described by Remsen & Dohme for the chloro-esters. After standing about two months however it was found that both of them had solidified to a semi-crystalline mass. They were washed as well as possible with absolute ether dried in a desiccator over concentrated sulphuric acid, and analyzed for chlorine & sulphur by the method of Carius. [illegible] [illegible] of chlorine were

found in each salt. Of the methyl salt,

0.2068 gr. gave 0.2227 gr. $BaSO_4$ = 14.79% S.

Of the ethyl salt,

0.2138 gr. gave 0.2093 gr. $BaSO_4$ = 13.46% S.

The formula $C_6H_4<{CO \cdot OCH_3 \atop SO_2 \cdot OH}$ requires 14.81% sulphur, and the formula $C_6H_4<{CO \cdot OC_2H_5 \atop SO_2 \cdot OH}$ 13.91% Sulphur.

Both salts are very hygroscopic and easily soluble in water giving acid solutions. It is evident, from these facts that the chlor-ester first formed had been further acted upon by the alcohols giving rise to acid esters according to the following reaction:

$$C_6H_4<{COOR \atop SO_2Cl} + 2ROH = C_6H_4<{COOR \atop SO_2OH} + HCl + R_2O.$$

In conclusion the author wishes to take this opportunity of expressing his sincere gratitude to Prof. Goessmann at whose suggestion and under whose constant supervision the work was carried on

John [illegible] [illegible] May, 18[illegible]

Biographical.

The author of this dissertation was born in Le Roy, Genesee County, New York April 3, 1869. His early education was received in public and in private schools of that town. In 1887 he entered Lafayette College at Easton, Pennsylvania, and received the degree of Bachelor of Arts in 1891 and Master of Arts in 1894. During 1891-92 he was private assistant to Dr. Wolcott Gibbs at Newport, R.I. and during 1892 + 93 he was Instructor in Analytical Chemistry in Pennsylvania State College, State College, Centre County Pa. In October 1893 he entered Johns Hopkins University as a student in Chemistry, Mineralogy, + Mathematics. During 1894-95 he also held the position of Demonstrator in Chemistry in the University of Maryland.